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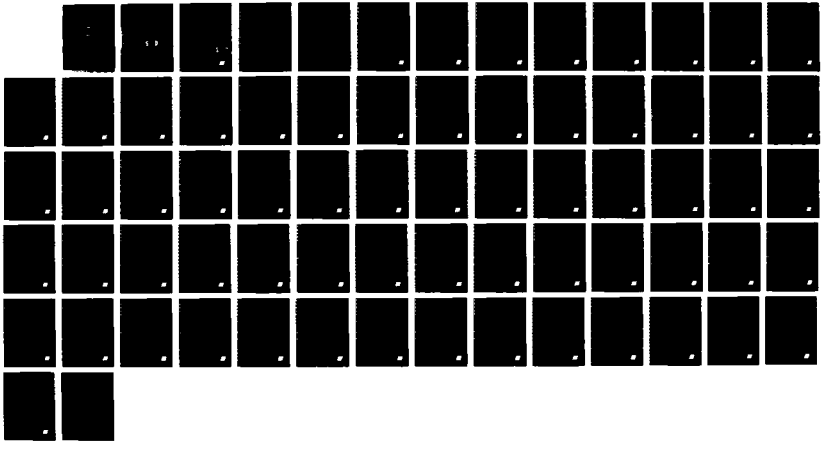

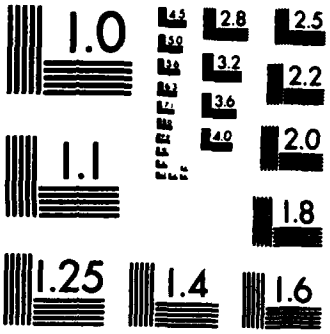

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This review covers the standard method of determining cetane number (engine test, ASTM D613) and alternative methods, which comprise 1 engine test method and 33 cetane indices (predictive equations of cetane number). Of the alternative methods, emphasis is given to those which appear or had appeared promising as good predictors of cetane number.

The various cetane indices are categorized according to the type of parameters employed viz, physical properties (e.g., the calculated cetane index, ASTM D976, an approved alternative method to ASTM D613), chemical composition/structure, and physico-chemical properties (e.g., spontaneous ignition tests). Of the physical properties, the combination of distillation temperature(s) and density appear to afford good correlations between cetane index and cetane number. Furthermore, these two parameters continue to feature in the replacement equations of D976. For indices based on a single property, aniline point gives the best prediction. (Keywords:

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A continuing need for the revision of ASTM D976 is indicative of changes in fuel composition. Consequently, cetane indices based on compositional analysis may be better predictors of cetane number than those based on physical properties.

Also, in this review, the effects of hydrocarbon structure on cetane number and spontaneous ignition, as well as the effect of low temperature on ignition quality are briefly addressed. Some recommendations regarding future work are also made.

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LIST OF SYMBOLS

(Symbols listed pertain only to those parameters commonly used in the various equations throughout the text.)

AP	Aniline Point in °C or °F, as specified (ASTM D611).
CN	Cetane Number (ASTM D613).
CI	Cetane Index.
CCI	Calculated Cetane Index (ASTM D976-80, unless otherwise stated).
D	Density at 15°C, g/mL (ASTM D1298).
G	API Gravity, °API (ASTM D287 or D1298).
H	Hydrogen content, wt% (ASTM D3701).
M	50% Distillation temperature *, °F, (ASTM D86).
PCN	Predicted Cetane Number.
T10	10% Distillation temperature *, °C (ASTM D86).
T50	50% Distillation temperature *, °C (ASTM D86, unless otherwise stated).
T90	90% Distillation temperature *, °C (ASTM D86).
Visc	Viscosity: at 40°C, cSt, unless otherwise stated (ASTM D445).
*	% Distillation Temperature refers to the distillation temperature of % recovered distillate.

1.0 PROJECT PLAN

Project: Cetane Number Correlations

Objective: Evaluate means of determining the cetane number from chemical or physical properties.

Approach:

1. Review literature thoroughly to establish what has been tried and with what success.

2. Propose experimental work to further established techniques or develop new correlations with simpler measurements.

3. Study the effect of hydrocarbon structure on cetane number and spontaneous ignition.

2.0 INTRODUCTION

Because of the demand for diesel fuel (a middle distillate fraction in the refining process), refineries use cracked stocks to increase the yield of middle distillates. Cracked stocks are blending streams produced by catalytic cracking processes. However, the use of cracked stocks increases the percentage of aromatics and naphthenic paraffins in the fuel blends. Furthermore, such types of compounds are known to lower the cetane number of distillate fuels.

Cetane number (C.N.) is a measure of the ignition quality of a diesel fuel in a compression-ignition engine. The term, ignition quality, refers to the ease with which a fuel will ignite, and is related to the ignition temperature and the ignition delay characteristics of the fuel. For example, the cold starting ability and engine roughness are related to the ignition delay characteristics of the fuel. The determination of cetane number is therefore important in characterizing the ignition performance of diesel fuels.

This literature review addresses Approach 1 of the Project Plan (see Section 1.0). In this presentation, the standard method for determining cetane number is first described along with problems associated with the method. This is followed by a review of alternative methods for determining ignition quality. In complying with the objective of this project, emphasis is given to those methods which appear promising in correlating physical or

chemical properties of the fuel with cetane number. Methods which give excellent correlation are needed for predictive purposes, particularly in the purchase of non-spec fuels.

The effect of hydrocarbon structure on cetane number and spontaneous ignition is included since it is pertinent to Approach 3. Furthermore, because starting at low ambient temperatures is difficult for low cetane number fuels, the the effect of low temperature on ignition quality is also included. Finally, based on the literature review, some suggestions for proposed experimental work are made (Approach 2, Section 1.0).

To aid the reader, symbols for parameters commonly used in the various equations throughout the text have been standardized (see List of Symbols, p. v). Consequently, these symbols may not be the same as those employed in the original formulations.

3.0 STANDARD METHOD OF DETERMINING CETANE NUMBER

Description

The standard method for determining cetane number is an engine test, ASTM D613 [1]. This test involves a single cylinder Waukesha Cooperative Fuels Research (CFR) engine. The fuel is injected using high pressure nozzles into hot compressed air, and the cetane number is a measure of the ease of compression ignition. Specifically, the compression ratio of the engine is varied to obtain an ignition delay of 13 crankangle degrees (13°CA).

Reference Fuels

The cetane number of a test fuel is determined by matching its compression ratio for ignition at 13°CA delay with the corresponding compression ratios of reference fuel blends of known cetane numbers, at the same 13°CA delay. Two primary reference fuels are cetane (hexadecane) and 1-methylnaphthalene; their cetane numbers are arbitrarily set values of 100 and zero, respectively [2]. Essentially, cetane number is the percentage by volume of cetane in that blend with 1-methylnaphthalene which gives the same ignition delay as the test fuel in the standard test engine [3a]. Since 1-methylnaphthalene is extremely difficult to compression ignite in the Waukesha engine, it has been replaced by 2,2,4,4,6,8,8-heptamethylnonane, which has a cetane number of 15 [4]. Also, because of the cost of high purity primary reference fuels, less costly secondary reference fuels have

been approved for use in the ASTM D613. These fuels are mixtures of hydrocarbons and are produced commercially. The high level cetane fuel is designated T-18 (cetane number, 75), and the low level cetane fuel is designated U-11 (cetane number, 20.5).

Problems

Problems associated with the ASTM D613 test method for determining cetane number include the following [5]:

1. Poor correlation of the test ignition characteristics with the ignition delays in production diesel engines.

2. Poor repeatability and reproducibility of the test data.

3. The test does not adequately detect small differences in cetane number at the lower range of the cetane scale, i.e., below 40 CN [6].

4. Fuel spray impingement on the hot cylinder walls decreases the ignition delay. Moreover, spray impingement occurs regardless of the compression ratio.

5. Tests are expensive and time consuming.

6. Engine and instrumentation are expensive.

However, cetane number is an important measure of ignition quality: it represents the total effects of spray formation, heating, vaporization, turbulent mixing, and chemical induction times under specified conditions of a single cylinder standard diesel engine [7]. Consequently, an ASTM Subcommittee (S.C.1 on Combustion Characteristics under Committee D-2) that is responsible for the Cetane Method, D613, has been working to address the various problems associated with the test method. Details of the positive approaches being considered have been outlined by Jones and Olsen [8].

4.0 ALTERNATIVE METHODS FOR DETERMINING CETANE NUMBER

These may be broadly categorized into two types, viz., engine and non-engine test methods.

4.1 Engine Test Method

This differs from the standard engine test method (ASTM D613) in that it involves the technique of engine throttling to misfire. This method, which was first published by Boerlage and Broeze [9] and later incorporated in a British Institute of Petroleum standard [10], is no longer widely used. Nevertheless, Johnston and Christie [11] have used a variation of the method to measure the cetane number of a variety of experimental materials including mono-esters of fatty acids, transesterified seedoils, hydro-treated aromatics, and fuels containing an alkyl nitrate combustion improver. Advantages of the method are as follows:

1. Only small quantities of fuel are required (~100 mL).

2. Any single cylinder may be used.

3. No sophisticated measuring equipment is necessary.

4. Test is rapid. This results in an added advantage, viz., the engine is not seriously fouled even with poor fuels.

5. Unlike the standard ASTM D613 procedure, there is no change of compression ratio, and the combustion chamber shape is fixed for all fuel comparisons.

6. The conditions of the engine throttling test are qualitatively similar to those brought about by lowering the compression ratio in an operating CFR engine.

7. The test may be used to determine the cetane quality of a wide range of liquid fuels with a reliability comparable with that of the 13° fixed delay method.

The many advantages of this method therefore merit further testing using diesel fuels which exhibit a wide range of cetane numbers (~25-60).

4.2 Non-Engine Test Methods

The ignition characteristics of a fuel are known to be related to its chemical composition [4, 5, 12, 13]. Furthermore, the chemical composition of the fuel governs its physical and chemical properties. Consequently, the various non-engine test methods for estimating cetane number may be classified on the bases of the following:

1. Physical properties of the fuel.
2. Chemical composition of the fuel, including the molecular structures of the fuel components.

3. **Physico-Chemical properties of the fuel, e.g., in the determination of spontaneous ignition and related methods; also, in thermogravimetry coupled with differential thermal analysis.**

These various methods are discussed in the following Sections.

4.2.1 *Methods Based on Physical Properties of the Fuel*

These include various predictive equations of cetane number, known as **cetane indices.** The indices are based on specific physical properties of the fuel. Furthermore, these properties are related to the chemical composition of the fuel. Examples of physical properties employed in the formulation of cetane indices and their relation to chemical composition of the fuel are as follows:

1. Density (API gravity) and aniline point: these are related to aromatic/paraffinic content and to a small extent, the degree of branchiness of the molecules [13].
2. Viscosity and density: these have been correlated with aromatic content [14].
3. Mid-boiling point: this is a measure of molecular size [4, 13].

Volatility, density, and viscosity of the fuel may also influence the physical processes that are involved in ignition, viz., vaporization of the fuel droplets to form a

flammable mixture. However, less volatile fuels have, in general, shorter ignition delays [12] and higher cetane numbers [15]. Murphy [15] has attributed this to a size effect i.e., larger molecules tend to be more fragile and therefore, more susceptible to thermal decomposition. In the case of viscosity, which may influence atomization of the fuel, fuel injection systems are capable of providing adequate atomization for fuels with viscosities in the range 0.5 to 8 centistokes [15].

Some of the important cetane indices that have been reported for estimating the cetane number of various types of diesel fuels are described next.

4.2.1.1 **Cetane Indices for Conventional Diesel Fuels** (E.g., straight run fuels, catalytically cracked stocks and blends of the two.)

A. *Diesel Index*

Initially, the diesel index [16], which was published in 1934, was very popular. It is calculated from the API gravity and aniline point of the fuel, the formula being:

$$\text{Diesel Index} = \frac{G * AP}{100} \qquad (1)$$

where:

G = API Gravity, °API
AP = Aniline Point, °F

B. *Calculated Cetane Index*

The need for greater accuracy in estimating cetane number led to the development of the calculated cetane index (ASTM D976-66/IP*218-66). The parameters involved are API gravity and 50% distillation temperature, the formula being:

Calculated Cetane Index (ASTM D976-66)

$$CCI = 0.49083 + 1.06577\ (X) - 0.0010552\ (X)^2 \qquad (2)$$

where:

$$X = 97.833\ (\log M)^2 + 2.2088\ G \log M + 0.01247\ G^2 - 423.51 \log M - 4.7808\ G + 419.59$$

M = 50% Distillation temperature, °F

Note: Instead of using equation 2, the calculated cetane index may be conveniently determined by means of the nomograph (alignment chart) shown in ASTM D976-66.

Revision of Calculated Cetane Index:

Because of dissatisfaction in the correlation between the calculated cetane index and cetane number, ASTM D976-66 was revised by an ASTM task force and replaced by ASTM D976-80 [17]. The new equation employs the same parameters as the old, but involves a different formula which is as follows:

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* Institute of Petroleum

Calculated cetane index (ASTM D976-80)

$$CCI = -420.34 + 0.016\,G^2 + 0.192\,G \log M + 65.01\,(\log M)^2 - 0.0001809\,M^2 \quad (3)$$

Alternatively, the calculated cetane index may be formulated as:

$$CCI = 454.74 - 1641.416\,D + 774.74\,D^2 - 0.554\,T50 + 97.803\,(\log T50)^2 \quad (4)$$

where D is the density at 15°C, g/mL, and T50 is the 50% distillation temperature, in °C.

Note: Instead of using equation 3 or 4, the revised calculated cetane index may also be conveniently determined by means of the nomograph shown in ASTM D976-80.

Because the revised equation (ASTM D976-80) was not necessarily an improvement for non-USA fuels, a test program was subsequently designed by the Institute of Petroleum to evaluate both the old and new equations using a large set of UK/European fuels. The results of this evaluation which have been reported by Thompson [17] of Shell Research Ltd., are as follows:

1. The new (revised) equation (ASTM D976-80) correlated better with C.N. for fuels with cetane numbers in the range 45-55.

2. The old equation (ASTM D976-66) was more accurate for fuels with cetane numbers in the 55-60 range.

In an attempt to improve on both the old and new equations, alternative prediction models were derived using linear regressions [17]. The best model obtained using aniline point data in addition to the original parameters (i.e., density and mid-boiling point) is as follows:

$$C.I. = 1.30 + (0.8848\ AP + 0.0947\ T50)/D - (0.9368\ AP*D) \quad (5)$$

where: CI = cetane index
AP = aniline point, °C

Two equations which did not employ aniline point data were also developed. The first is as follows:

$$C.I. = 81.18 + (0.1399\ T50)/D - 108.31\ D^2 \quad (6)$$

The second equation is not shown because of inaccuracies in the published formulation [17]. However, this second equation was developed to overcome the problem of bias relating to the cetane of the sample. Nevertheless, for the cetane number range, 40-55, none of the equations formulated were improved models of ASTM D976-80. Consequently, ASTM D976-80 was recommended for adoption as an Institute of Petroleum (IP) procedure [17].

The calculated cetane index is the most widely used method for predicting cetane number [15]. Although specification requirements for ignition quality are defined in cetane numbers, most specifications permit the use of the calculated cetane index as an approximation of cetane number

[17]. In cases of disagreement, however, cetane number is used as the referee method. Nevertheless, two types of problems are associated with the calculated cetane index. These are described next.

Problems Associated with the Calculated Cetane Index:

1. *Inherent Limitations*

As described in the ASTM Method, D976-80, inherent limitations of the calculated cetane index equation are its inapplicability to the following:

a) Fuels containing additives for raising cetane number.

b) Pure hydrocarbons, synthetic fuels such as certain products derived from shale oils and tar sands, alkylates, or coal tar products.

c) Crude oils, residuals, or products whose distillation end points are below 500°F.

2. *Biases*

Although the calculated cetane index is generally a reliable method for predicting the cetane numbers of standard diesel fuels, biases do occur (i.e., over/under prediction). For example, Canadian refiners have found that both ASTM D976-66 and D976-80 overpredict the cetane numbers

of their fuels. In contrast, British and Australian users of D976-80 have found the equation underpredicts on their diesel fuels. Also, these biases have been found to vary with cetane number [6].

C. Improved Cetane Indices

To address the problem of biases associated with the calculated cetane index, as well as some of its inherent limitations, various predictive equations of cetane number have been developed. One of these is currently being balloted to replace the D976-80 (see Section 4.2.1.3 B). Both the D976-80, and the currently balloted equation (see equation 19) employ similar parameters as the original calculated cetane index (976-66). However, of the revised calculated cetane indices, equation 19 is more complicated that D976-80 and employs additional distillation temperatures data.

The various predictive equations are reviewed as follows: Cetane indices for petroleum-derived diesel fuels are described below. A cetane index for alternative fuels is described in Section 4.2.1.2. Cetane indices for both conventional and synthetic diesel fuels are described in Section 4.2.1.3. Finally, cetane indices for residual fuels are described in Section 4.2.1.4.

1. *Collins and Unzelman Improved Equations*

These equations [6] involve correction factors, or new correlations, or both, as well as an equation for diesel fuels containing ignition improvers, and are as follows:

a) Correction Factors:

i) For ASTM D976-80

$$PCN = 21.843 - 0.33924(CCI) + 0.018669(CCI)^2 \quad (7)$$

where:

PCN = Predicted Cetane Number

ii) For New Cetane Index - Note: This new cetane index, which is defined below, involves the same physical properties as D976-80)

$$PCN = 12.822 + 0.1164\ (CI) + 0.012976\ (CI)^2 \quad (8)$$

where:

$$CI = 0.9187\left(\frac{G}{10}\right)^{1.26687}\left(\frac{M}{100}\right)^{1.44227}$$

b) New Correlations Based on Aniline Point

$$PCN = 18.196 - 1.254\left(\frac{AP}{100}\right) + 14.34\left(\frac{AP}{100}\right)^2 \quad (9)$$

$$PCN = 16.419 - 1.1332\left(\frac{AP}{100}\right) + 12.9676\left(\frac{AP}{100}\right)^2 - 0.2050\left(\frac{AP}{100}\right)^3 + 1.1723\left(\frac{AP}{100}\right)^4 \quad (10)$$

where: AP = Aniline Pt. in °F

c) Cetane Number Improvememt (CNI) Equation:

$$CNI = 0.17402\left(\frac{G}{10}\right)^{1.4444}\left(\frac{M}{100}\right)^{1.0052}$$

$$[\ln (1 + 17.5534I)] \qquad (11)$$

where: I = Vol % of diesel ignition improver

Note: In equation 11, as you would expect, when the ignition improver concentration is zero, the cetane number improvement is also zero.

Of equations 7-10, equation 8 was marginally better than equation 7, and equation 10 was a definite improvement over equations 7, 8 and ASTM D976-80. The main set of fuels examined in this study comprised the 1208 distillate fuels used in the development of the ASTM D976-80 equation. Also included in the study were the following: data on a set of 45 blends of European quality diesel fuels, 27 fuels (with measured cetane numbers and containing no ignition improvers) taken from a 1980 U.S. Department of Energy report [18], and 76 Canadian diesel fuels.

2. *Ethyl Corp. Equation (Michalski and Unzelman [19])*

This involves a different correction factor for the calculated cetane index (cf. equation 7) and is as follows:

$$PCN = 5.28 + 0.371\ (CCI) + 0.0112\ (CCI)^2 \qquad (12)$$

The Ethyl equation was developed from a large data base and was designated the best of those reviewed by the ASTM Cetane Prediction Task Force in early 1983 [20].

3. *Ethyl Corp. Aniline Point Equation (Unzelman [21]).*

$$PCN = 0.00143\ (AP)^2 + 16.537 \qquad (13)$$

where: AP = Aniline Point in °F.

This equation is much simpler than equation 10, but was developed especially for light cycle oils. However, problems with using aniline point as a predictor include the loss of accuracy with heavy dark-colored fractions [20], wide variation in the results unless freshly distilled aniline is used, and the toxicity of aniline [6].

4.2.1.2 Cetane Index for Alternative Fuels (E.g.,synthetic fuels)

Murphy's Predicted Cetane Number

To address the need for a predictive equation for alternative fuels, Murphy [15] has proposed an equation that is based on 50% distillation temperature, density and percent hydrogen of the fuel. The equation, which was derived using least squares multiple regression analyses of cetane number versus properties of the fuel, is as follows:

Predicted Cetane Number =

$$21.56 \ln T50 - 59.346 |D - 0.835| + 75.455 \ln H - 265.2 \quad (14)$$

where: H = hydrogen content of fuel, wt %.

Note: The 2 parallel lines enclosing the density term refer to its absolute value i.e., the term within these lines is always positive. This density term is based on the observation [15] that for density values less than 0.835 g/mL, cetane number increases with density; whereas for density values greater than 0.835 g/mL, cetane number decreases with increasing density.

Of the above three fuel properties, Murphy [15] found that hydrogen content had the greatest effect on the predictive equation. Also, in a study of 74 fuels including alternative and unusual diesel fuels, the average error of Murphy's predictive equation was less than two thirds that of ASTM D976-80.

4.2.1.3. Cetane Indices for Both Synthetic and Conventional Diesel Fuels

A. *Canadian General Standards Board (CGSB) Cetane Index*

The CGSB cetane index [22] was developed because of the need for an index which would predict the cetane number of synthetic diesel fuels equally as well as it would

conventional diesel fuels (i.e., petroleum distillates). The proposed equation is based on aniline point, distillation range, density, and viscosity:

$$\text{Cetane Index} = 77.7628 + 0.1765\ AP + 0.003867\ (AP)^2 - 11.6150\ K_C + 0.5844\ K_C^2 - 0.6350\ Visc \quad (15)$$

where: AP = Aniline Point in °C

$$K_C = \frac{T10 + T50 + T90 + 820}{200\ D^2}$$

T10, T50, and T90 refer to the distillation temperatures in °C of 10%, 50% and 90% of recovered distillate

Visc = Viscosity in cST at 40°C

Because some labs indicated a possible problem with the routine use of aniline, another index which did not employ aniline point was developed. The best non-aniline point index proposed is as follows:

$$C.I. = 185.551 + 2.358\ K_C^2 - 39.157\ K_C + 0.000276\ H \quad (16)$$

Equation 16 however, is a poorer predictor of cetane number than equation 15. Since hydrogen content is not readily run at all laboratories, a second best non-aniline point equation was formulated:

$$C.I. = 183.229 + 2.437\ K_C^2 - 39.678\ K_C \quad (17)$$

Advantages of equation 17 are its simplicity, and that it needs only two fuel inspection tests, viz., density and D86 distillation.

In an extensive study involving 74 Canadian fuel samples, all 3 equations, i.e., 15, 16 and 17, predicted cetane number better than the current and old ASTM indices (ASTM D976-80 and D976-66 respectively). The equations were derived using least squares computer regression analyses of the fuel properties versus the average cetane number of the fuel.

The fuel samples used in this project, were obtained from Texaco Canada Inc., Shell Canada Ltd., Gulf Oil Canada Ltd., Esso Petroleum Canada, and Petro-Canada Ltd. (formerly B.P Canada Ltd.). Also, the fuels were from production as well as from laboratory blends covering the cetane number range 30 to 55.

Equation 15 was found to predict the cetane number of diesel fuels containing synthetic distillates equally as well as it did conventional petroleum distillates. Furthermore, this equation is currently in use by a number of Canadian refiners and is expected very shortly to receive full Petroleum Committee approval as a CGSB Test Method.

B. *Ingham, Bert and Painter Improved equations* (Chevron Research Co.)

Ingham et al. [23] have recently developed three predictive equations for cetane number. Each of these equations was found to be an improvement in predictive accuracy relative to ASTM D976-80 equation. These results were based on 1229 fuels comprising commercial diesel fuels, refinery blending components, and synthetic fuels derived from coal, shale and tar sands. The commercial diesel fuels were from various oil companies including Shell, Texaco Beacon Laboratory, Amoco U.S.A, Ethyl U.S.A., Ethyl Europe, Sohio U.S.A., Exxon U.S.A., and Williams Oil Company.

The parameters involved in the three equations include the following:

a) Aniline Point (equation 18).

b) Distillation Temperatures (T10, T50, T90) and density (equation 19)

c) Distillation temperatures (T10, T50, T90) density, and aniline point (equation 20).

where: Aniline Point (AP) is in °C

In the equations which follow, the suffix N of the physical properties parameters (i.e., PCN excluded), refers to normalization. This was done to minimize the correlation

between the independent variables, and was performed by subtracting from each observed value, the mean of that term for the data set [23].

a) Aniline Point Equation

$$PCN = -0.611 + 45.5*EXP(0.0150 * APN) \quad (18)$$

where:

$$APN = (AP - 60)$$

b) Mid-boiling Point and Density Equation.

$$PCN = 45.2 + 0.0892*T10N + (0.131 + 0.901 * C)*T50N + (0.0523 - 0.420 * C)*T90N + 4.90E-4*(T10N^2 - T90N^2) + 107*C + 60.0*C^2 \quad (19)$$

where:

$$C = EXP(-3.50 * DN) - 1$$

$$DN = (D - 0.850)$$

$$T10N = (T10 - 215)$$

$$T50N = (T50 - 260)$$

$$T90N = (T90 - 310)$$

c) Mid-boiling Point, density, and Aniline Point Equation

$$PCN = 44.9 + 0.0376 * T10N + (0.0637 + 0.620 * C) * T50N + (0.0118 - 0.241 * C) * T90N - 7.40E-4 * T90N^2 + 50.7 * C + 132 * C^2 + (0.382 + 0.00238 * VN) * APN$$

where: (20)

$$VN = V - 260$$

$$V = (T10 + T50 + T90)/3$$

Equation 20 was the best predictive equation developed: its standard error of prediction was 30% less than that of D976-80. For equations 19 and 18, the corresponding standard error of prediction values were respectively, ~25% and 17% less than that of D976-80. However, because of the toxicity of aniline, equation 19 has been selected instead for balloting by ASTM as a replacement for D976-80.

C. *National Research Council of Canada (NRCC) Cetane Index*

This extremely complex equation by Gülder et al. [13] (see equation 21) employs similar parameters as the CGSB cetane index (see equation 15) viz., distillation temperatures, density, aniline point, and viscosity. In formulating the NRCC cetane index, Gülder et al. [13] used certain relationships which they had established between physical properties and chemical structures of the fuel. The NRCC cetane index was derived from a data base of 394 fuels comprising commercial diesel fuels without ignition improvers, fuels from tar sands, coal-liquid blends, heavy residual blends and light heating oil blends, as well as the fuel set used in the CGSB study.

$$PCN = 11.113Y_1 - 0.3175Y_2^2 - 391.644\ (1/Y_2) + 269.14D^2 + 10.881\ (Y_4/D)^2 - 719.41\ (D/Y_4) + 612.473\ (1/Y_3^2) + 1727.94\ (1/Y_4) - 949.466\ (1/Y_4^2) + 0.0223\ Visc + 11.425\ (1/Visc) + 8.19 \ln [(Y_3 - Y_4)^2] + 5.181\ [(Y_3 D)/Y_4]^2 + 15.365\ (AP/50) + 4.23\ (AP/50)^2 - 595.3 \quad (21)$$

where:

$Y_1 = Tm/D^2$ (this ratio was found to be related to cetane number at constant carbon aromaticity).

$$Tm = \frac{T_{10} + T_{50} + T_{90}}{300}$$

$Y_2 = Tm^2/D$ (this ratio was found to be related to the ratio of straight chain paraffinic groups to branched groups at constant carbon aromaticity).

$Y_3 = T_{90}/100D$ (this ratio was found to be related to the relative amount of straight chain paraffins and n-paraffinic substitution to aromatic rings, at constant carbon aromaticity).

$Y_4 = T_{10}/100D$ (this ratio was found to be related to the branchiness of the fuel components at constant carbon aromaticity).

$Y_3 - Y_4$, and Y_3/Y_4 are related to the skewness of the carbon number distribution of hydrocarbons in the fuel.

In a comparison of the NRCC cetane index with several promising cetane indices (viz, Ingham's equation (equation 19), the CGSB cetane index, Ethyl equation and ASTM D976-80),

Gülder et al. [13] found their equation to be a better predictor of cetane number. However, the complexity of the NRCC cetane index detracts from its merits. Nevertheless, the systematic approach taken by Gülder et al. [13] is significant, since it addresses for the first time, the correlation between cetane number and certain functions of physical properties which are related to compositional analysis.

4.2.1.4 Cetane Indices for Residual Fuels

A. *Shell Calculated Carbon Aromaticity Index (CCAI)*

This index is based on the density and kinematic viscosity of the fuel, the formula being:

$$CCAI = D - 140.7 \log \log (Visc + 0.85) - 80.6 \quad (22)$$

where: Visc = kinematic viscosity in cSt at 50°C.

In a study of 19 fuels comprising distillate and residual fuels, Zeelenberg, et al. [14] obtained a correlation between CCAI and ignition delay.

B. *Calculated Ignition Index (CII)*

David and Denham [2] derived two predictive equations for determining the cetane number of residual fuels. These equations, referred to as calculated ignition index 1 and 2, were derived using linear regression analysis of the

physical properties data versus ignition number. CII-1 is based on density and viscosity, and its correlation coefficient compares well with that of the calculated carbon aromaticity index (equation 22). CII-2 is based on density and aniline point, and its correlation coefficient is similar to that of the diesel index. These equations are as follows:

$$CII\text{-}1 = 294.26 - 277.30D + 13.263 \log \log (Visc + 0.7) \quad (23)$$

$$CII\text{-}2 = (64.024/D^2) + 0.00122AP^2 - 46.36 \quad (24)$$

where: Visc = kinematic viscosity at 100°C (cSt)
AP = aniline point (°C).

In a study of 45 residual fuels, comprising straight-run atmospheric residues, visbroken residues and residue/diluent interfuel blends, good correlation between the measured ignition number and the calculated index was obtained with both equations.

4.2.2 Methods Based on Chemical Composition/Structure of Fuel Components

As mentioned earlier (Section 4.2), the ignition characteristics of a fuel are related to its chemical composition. Specifically, the molecular structures of the fuel components are important. For example, long straight chain paraffins (e.g., hexadecane) have high cetane numbers, whereas, branched paraffins (e.g., 2,2,4,4,6,

8,8-heptamethylnonane), cycloalkanes, and aromatics (e.g., 1-methylnaphthalene) have low cetane numbers [4, 5, 12]. Also, alkenes have slightly lower cetane number than their corresponding alkanes [4, 5]. The various expressions for estimating cetane number based on the molecular structures of the fuel components are described in the following sections.

4.2.2.1 Correlations Based on %-Paraffins, Naphthenes and Aromatics:

Based on the percentages of paraffins, naphthenes, and aromatics present, Kreulen [24], and Backhouse and Ham [25] have proposed formulas for predicting the ignition quality of diesel fuels. Kreulen's formula for calculating cetene value* from the carbon distribution is as follows:

$$\text{Cetene Value} = 0.85\ C_P + 0.1\ C_N - 0.2\ C_{Ar} \qquad (25)$$

where C_P, C_N, and C_{Ar} represent the mole percents of paraffinic, naphthenic, and aromatic carbons, respectively.

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*The term cetene number is found in the old literature, and is based on a scale with cetene defined as 100. Cetene number = 0.875 cetane number.

In a study involving 11 gas oils (cetene value range: 23.5 to 65), Kreulen [24] obtained good correlation between the measured cetene value (engine test) and the calculated value for 9 oils. However, the correlation was poor for the remaining 2 oils. Of these, one case was attributed to the presence of iso-paraffins which are not accounted for in his equation, but no explanation was offered for the other case.

Also, Backhouse and Ham [25] tried to show that for all saturated fractions the ratio of the percentage of paraffinic carbon to cetane number is almost constant.

4.2.2.2 Correlation Based on H/C Ratio

Kondo, et al. [26] have shown a linear relationship between cetane number and the H/C ratio of the mixtures of hydro-treated coal derivatives and commercial diesel fuels.

For a small number of selected fuels, these correlations [24-26] can be claimed as being successful [5]. However, for statistically acceptable number of fuels, these correlations have been found to be inadequate [5, 27].

4.2.2.3 Correlation Based on Number of Specific Types of Hydrogen

Ohuchi, et al. [28] have shown a relationship between the cetane number and the number of hydrogen atoms at beta-

and farther positions to the aromatic ring, excluding terminal methyl groups. Nevertheless, their data also showed a large degree of scatter, i.e., the cetane number spread for a given hydrogen count varied as much as 20 points.

4.2.2.4 Correlations Based on Carbon Type Structure

A. *From the National Research Council of Canada*

Glavincevski, et al. [27] have reported that the above mentioned poor correlations were attributable to the lack of a term (or terms) which represent(s) the different type of paraffins, e.g., normal and iso-alkanes. Furthermore, these authors [5, 7, 27] have derived various correlation expressions based on multiple regression analysis for the prediction of cetane numbers of diesel fuels. A large number of diesel fuels (~67 to 134) were examined, and their ignition quality covered a broad range of cetane numbers (20 to 75).

The initial correlations of Glavincevski, et al. [27] were based on the carbon type structure obtained from proton NMR analysis of 134 fuels. These fuels comprised a wide range of conventional and diesel fuels including fuels from tar sands and those containing heavy residuals and light heating oil. In their proposed correlations (given below), the various types of carbons identified are as described.

$$PCN = A_o + \frac{A_1}{C_A} + A_2 C_A^{1.5} + A_3 C_\alpha$$

$$+ A_4 \ln C_\alpha + A_5 C_2 + A_6 C_3 \qquad (26)$$

where:

$A_o = 111.2387$, $A_1 = -28.2098$
$A_2 = -0.1048$, $A_3 = -1.1533$
$A_4 = -7.811$, $A_5 = 0.0853$
$A_6 = -1.5036$

C_α = aromatic ring carbons substituted by alkyl groups; the number of these carbon types are equivalent to the α-alkyl hydrogen integral divided by 2.5

C_A = aromatic carbon atoms
= $1.4\ (H_{dar}) + H_{mar} + C_\alpha$: H_{dar} are the hydrogens on condensed di- and poly-aromatic rings; and H_{mar} are the hydrogens on mono-aromatic rings.

C_2 = methylene carbons

C_3 = methyl carbons

Note: The sum of the relative number of carbon atoms of each region is normalized so that: $C_A + C_2 + C_3 = 100$.

For a quick estimation, a simpler equation (equation 27) was derived, but its accuracy was not as good as that of equation 26:

$$PCN = B_o + \frac{B_1}{C_A} + B_2 C_2 + B_3 C_3 \qquad (27)$$

where:

$B_o = -1.6750$, $B_1 = 21.8710$
$B_2 = 1.0819$, $B_3 = -0.2614$

Glavincevski, et al. [27] found that the error in the estimated cetane number of equation 26 was smaller than the spread of cetane numbers determined on a number of engines (~11 to 20). Nevertheless, to further reduce the errors involved in the correlations, equation 28 (shown below) was proposed by Gülder and Glavincevski [5], and is based on the analysis of 67 fuels.

$$PCN = B_o + \frac{B_1}{C_A} + \frac{B_2}{C_A^2} + (B_3 C_\alpha + B_4 \ln C_\alpha) + (B_5 C_2 + B_6 C_2^2) + (B_7 C_3 + B_8 C_3^2) \quad (28)$$

where:

$B_o = 24.3848$ $B_1 = -286.728$ $B_2 = 587.3567$
$B_3 = 1.5227$ $B_4 = -15.882$ $B_5 = 0.9778$
$B_6 = 0.0047$ $B_7 = -0.2835$ $B_8 = 0.002$

These authors [5] found excellent agreement between the predicted and the observed cetane numbers. The correlation coefficient was 0.992 with a standard deviation of 1.11. In comparison with the correlation coefficient of the calculated cetane index with cetane number, which is 0.8628, this correlation coefficient is improved.

B. *From Exxon Research and Engineering Company*

DeFries, et al. [29] also developed a correlation between cetane number and the carbon type structure based on group additivity. The concept of group additivity assumes, as a first approximation, that many molecular properties are additive contributions of the properties of parts of the molecule [29]. The various types of carbons were identified using carbon-13 NMR spectroscopy. The advantages of carbon-13 versus proton NMR are that it provides information on long, medium, and short length chain effects on cetane number [29b]. Of the paraffinic carbons, six types were identified viz., methyl, methyne, quaternary, methylene gamma- or further away, methylene beta-, and methylene alpha- to a carbon atom which is not a methylene.

In a study of 34 paraffin compounds, the cetane numbers were regressed against the fraction of carbon atoms in each region. This simple correlation was found to give a very good fit [29a]. Also, in a study of 93 different hydrocarbon mixtures in which the cetane numbers were regressed against the fraction of total spectral area in each region of the spectrum, a good fit $R^2 = 0.98$ was also obtained [29b].

4.2.2.5 Correlations Based on Hydrogen Type Distribution

A. *From the National Research Council of Canada*

Gülder and Glavincevski [7] have recently reported that a correlation derived from hydrogen type distribution based on proton NMR analysis was more accurate in predicting ignition quality than their previous correlations derived from carbon type structure. The various types of hydrogens identified were the same as those employed in identifying the various types of carbons. These are designated as follows:

H_{a1}	hydrogens on condensed aromatic rings
H_{a2}	hydrogens on monoaromatic rings
H_{α}	hydrogens on α-position to aromatic rings
H_{CH_1}	hydrogens at β-position to aromatic rings, and naphthenic and paraffinic CH hydrogens
H_{CH_2}	paraffinic CH_2 group hydrogens, and hydrogens of CH_3 groups at β-position, CH_2 groups of γ-position or at positions further from aromatic rings
H_{CH_3}	hydrogens at paraffinic CH_3 groups and of CH_3 groups at γ- or positions further from aromatic rings

NB. The relative number of hydrogen atoms of each region was normalized such that their sum was 100. Consequently, in the equation which follows, the above symbols refer to % hydrogen type based on the total number of hydrogens.

$$PCN = A_o + \sum_{k=1}^{n} F_k(H_i) \qquad (29)$$

where:

$$F_1 = \frac{A_1}{H_{a1}} + \frac{A_2}{(H_{a1}+H_{a2})^4}$$

$$F_2 = \frac{A_3}{H_{a2}} + \frac{A_4}{(H_{a2})^2} + A_5(H_{a1})^{1.5} + A_6(H_{a2})^{0.5}$$

$$F_3 = A_7 H_\alpha + A_8 \ln H_\alpha$$

$$F_4 = A_9 H_{CH_1} + A_{10}(H_{CH_2})^{0.5} + A_{11} H_{CH_2}$$

and $$F_5 = A_{12} H_{CH_3} + A_{13}(H_{CH_3})^{0.5}$$

The following values for A_i have been determined as a result of a multiple regression analysis:

$A_1 = 0.0165$, $A_2 = 10.8428$
$A_3 = 18.4686$, $A_4 = -9.0653$
$A_5 = -0.2175$, $A_6 = 0.3909$
$A_7 = -0.2254$, $A_8 = -3.7344$

$A_9 = -0.3152$, $A_{10} = 17.1928$

$A_{11} = -0.7688$, $A_{12} = -1.6835$

$A_{13} = 13.6658$, $A_0 = -48.4907$

In a study of 70 diesel type fuels, the correlation coefficient was 0.994, and the standard deviation of residuals was 0.998.

B. *From Southwest Research Institute*

Bailey, et al. [30] also recently reported a good correlation between hydrogen type distribution based on proton NMR analysis and cetane number for various types of fuels viz., primary and secondary reference fuels, commercial fuels, and pure compounds. Compared to the very complex equation of Gülder and Glavincevski [7], which involves 14 coefficients, two relatively simple equations were developed using independent stepwise linear regression analysis.

One equation was for aromatic fuels or fuels containing some aromatics and is as follows:

$$PCN = 9.49 - 0.0298(D*H*H_{CH_3}) + 0.0896(D*H*H_{CH_2}) + 0.000097(D*H*S^2) - 0.038(D*H*H_{\alpha}) \quad (30)$$

where:

H_{CH_3} = % methyl hydrogen
H_{CH_2} = % methylene hydrogen
H_{CH_1} = % methine hydrogen
S = % (H_{CH_3} + H_{CH_2} + H_{CH_1})
H_α = % alpha hydrogen (hydrogens immediately adjacent to an aromatic ring)

Note: All percentages are based on the total number of hydrogens. Also the various hydrogen types identified are the same as those employed by Gülder and Glavincevski [7] (see p. 34).

The other equation was for non-aromatic hydrocarbon fuels and is as follows:

$$PCN = -54.00 + 1.018(D*H*H_{CH_1}) + 0.1595(D*H*H_{CH_2}) \quad (31)$$

The authors [30] claim that this approach, i.e., the product of three terms viz., density x wt % hydrogen content x % specific type proton of total protons, improves the prediction model. Density of the fuel was included since this was found to improve the modeling capability of the NMR parameters.

Disadvantages of all carbon type [5, 27, 29] and all hydrogen type [7, 30] correlation expressions are as follows:

1. Depending on the fuel composition, overlap of several chemical structure types in the same NMR spectral region can cause anomalous results, e.g., high concentrations of beta-methyl groups may not agree with the model [30].

2. The expressions do not take into account the presence of sulfur, nitrogen, or oxygen type compound in the fuels. This is important since these atoms can greatly affect the cetane number [29], e.g., alkyl nitrate is a cetane number improver [31]. Also, sulfur compounds, particularly disulfides and polysulfides, increase the cetane number of the base fuel [32].

4.2.3 *Methods Based on Physico-Chemical Properties of the Fuel*

4.2.3.1 **Spontaneous Ignition (Also referred to as autogeneous ignition or autoignition)**

Although, both physical and chemical properties of the fuel are involved in spontaneous ignition, the fuel's chemical properties are of greater significance (see Section 5.2). Spontaneous ignition studies involve measurement of the spontaneous ignition temperature as well as the ignition delay. Spontaneous ignition temperature of a fuel is the lowest temperature at which the fuel will

ignite in air in the absence of a spark or flame. The ignition delay is the time lapse between introduction of the fuel and actual ignition. These two parameters viz., ignition temperature and ignition delay are similar to those involved in the cetane number engine test ASTM D613.

Many research workers have obtained a fairly good correlation of cetane number with spontaneous ignition tests involving bomb techniques (3b). However, others have reported that the correlations of engine fuel performance with laboratory determined ignition delay data are imperfect [33] or of little value [34]. Furthermore, Clerget [35] showed that the relation between ignition delay and cetane number of nine fuels was not linear, even when ignition delay was measured under engine conditions. Also, Dumanois and Desbrosse [36] suggested the relation between ignition delay (t) and the cetane number (CN) was of the form:

$$CN(t - a) = b \qquad (32)$$

where a and b are constants.

At the Naval Research Laboratory, extensive research on autoignition of diesel fuels and pure hydrocarbons have been conducted. Using a modified Jentzsch ignition tester, Johnson et al. [37] found that the self-ignition point (i.e., the lowest temperature at which a drop of fuel will ignite when oxygen is being supplied at the rate of about 25 mL per minute [37]) is inversely related to cetane

number, i.e., the higher the cetane number, the lower the self ignition point (SIP). The same correlation was also observed for fuels containing ignition improvers.

However, these authors [37] found considerable deviations for individual fuels. In addition, SIP values for blends of n-cetane and 1-methylnaphthalene were found to be considerably higher than for fuels of comparable cetane numbers. These anomalies were attributed to pressure differences in the two tests i.e., SIP is determined at 1 atmosphere pressure, whereas in the engine test, ignition occurs at many atmospheres pressure.

Johnson et al. [37] also found ignition delay to be inversely related to cetane number i.e., ignition delay increases with decreasing cetane number. However, at a given temperature, the correlation between ignition delay and cetane number was poor. In an attempt to correlate the spontaneous ignition temperature at a fixed ignition delay with cetane number, similar scatter in the data was obtained as in SIP versus cetane number. The authors [37] have suggested that application to SIP of a correction factor based on other measured fuel properties might give a value that is more closely related to the cetane number. Grellin et al. [38] and Murphy [15] have also suggested similar modes of improving the correlation between the autoignition test and cetane number.

4.2.3.2 Minimum Ignition Point

In a further attempt to correlate the ignition characteristics of a fuel, as determined by a laboratory/ bench test method, with cetane number, the minimum ignition point (MIP) of the fuel was employed [38, 39]. MIP is defined as the lowest temperature for ignition in pure oxygen and includes cool flames. Note, the distinction between SIP and MIP is that SIP involves hot flames. Also, since cool flames are precursors of hot flame ignitions, transitions to hot flames can easily occur. Consequently, either type of ignition should be considered as positive ignition [39, 40].

In a study involving several olefins, cyclo-alkanes, n-paraffins and iso-paraffins as well as blends of primary reference fuels, Crellin et al. [38] found that MIP of the reference fuel blends was inversely related to cetane number. Furthermore, correlation between MIP and cetane number was generally good for the alpha-olefins and the cyclo-alkanes, but was poor for the n-paraffins.

Similar differences in correlation due to differences in structural types of the hydrocarbons were also shown by Crellin et al. [38] using Jackson's data [41]. Thus in a plot of Jackson's SIT values versus cetane number, for equivalent cetane number, the n-paraffins exhibited lower SIT values than the alpha-olefins.

Also, using the constant-volume bomb, Hurn and Smith [33] found that in a plot of cetane number versus ignition delay at 1000°F and 300 psi, the alpha-olefins and n-paraffins are both different from the primary reference fuel blends. These authors [33] attributed the differences in correlation for different structural types of hydrocarbons to different pressure and temperature sensitivities of these materials. Consequently, Crellin et al. [38] concluded that a simple bench-type ignition test such as MIP is not amenable to a strict correlation with an engine test such as cetane number.

However, the determination of cetane number of diesel fuels based on autoignition temperature of the test sample in a modified Moore instrument has been proposed by Azev et al. [42]. The method appears promising except for long test times. Also, extensive testing on a large number of fuels has not been conducted.

Ryan [43] from Southwest Research Institute has recently reported that ignition delay times measured using a combustion bomb apparatus correlated highly with cetane number, for petroleum derived fuels. However, for alternative and highly hydrotreated fuels the correlation was not as good.

Some of the problems involved in autoignition studies are as follows:

1. Spontaneous or autogeneous ignition temperature is an empirical value [44]. It varies with the surface-volume ratio of the container [45], the test pressure, and the fuel-oxygen ratio [40, 44]. Consequently, spontaneous ignition temperature values of the same fuel can vary depending on the apparatus, the method, as well as a combination of both of these [40]. This is important when comparing spontaneous ignition temperature data in the literature.

2. In the measurement of ignition delay, i.e., the induction period, false negatives may be recorded because of long ignition delays e.g., ignition delay of cyclohexane at 258°C was ~9 minutes [46]. However, a plot of ignition delay time versus temperature is useful in determining autoignition temperature [40].

4.2.3.3 **Partial Oxidation**

Chen [47] has reported a correlation between the heat released from partial oxidation of diesel fuels and cetane number. Heat release was monitored using a Foxboro Octane Analyzer, and the fuels examined included 4 blends of secondary reference diesel fuels, and 21 commercial diesel fuels. However, when the equation of simple regression was used to predict the cetane number of each fuel, the correlation between the predicted and actual cetane number

was not very good. The correlation coefficient was 0.7378, whereas that for cetane index versus actual cetane number is 0.8628. To improve the correlation, Chen suggested that the differences in physical properties of the fuel should be compensated for.

4.2.3.4 Thermogravimetry (TG)

Liddy [48] has applied the technique of TG coupled with differential thermal analysis (DTA) to the study of the ignition and combustion behaviour of several residual fuels. TG-DTA is a laboratory technique which yields information on mass loss and heat release rates of small samples (approx. 25 mg) as the sample is being heated.

Results of the study indicated that TG-DTA showed promise as a means of characterizing the ignition and combustion behaviour of residual fuels. Also, Liddy has reported that information on residue formation and burnout obtained from the TG trace should provide an indication of any anomalous behaviour likely to give rise to combustion problems in an engine. Nevertheless, Liddy has stressed that this experimental approach was not an attempt to simulate conditions in an engine cylinder. Instead, it was an attempt to measure aspects of fuel behaviour which can be related to fuel performance in an engine.

5.0 EFFECT OF HYDROCARBON STRUCTURE ON CETANE NUMBER AND SPONTANEOUS IGNITION

5.1 Effects of Structure

Hydrocarbon structure is known to influence both cetane number [5, 12, 27] and spontaneous ignition [37-39, 46, 49-51]. In the case of cetane number, Olson et al. [12] obtained the following results:

1. a) Increasing the chain length of normal paraffins (from pentane to hexadecane) increased the cetane number.
   b) Branching decreased the cetane number of paraffins.

2. a) Aromatics exhibited lower cetane numbers than the straight chain paraffins.
   b) An aromatic with three-carbon atom side chain is the most stable normal alkyl benzene i.e., ignition delay was longest for n-propylbenzene than for any other alkyl benzenes tested.
   c) Position of substituents on the benzene ring was also important. E.g., 1,4 - Dimethyl-benzene exhibited a lower cetane number than 1,2- and 1,3- dimethylbenzenes.

3. It was difficult to correlate the data on olefins with cetane number because of inconsistencies.

In the case of spontaneous ignition, Johnson et al. [49] showed that the self-ignition point (see Section 4.2.3.1) of pure hydrocarbons increased with the introduction of a double bond, shortening the carbon chain, and cyclization. In a continuing study, Johnson et al. [39] found that the minimum ignition point (see Section 4.2.3.2) of isomeric hexanes increased with the extent of branching. Affens et al. [46] also showed that the minimum ignition temperature for cool or hot flame ignition increased with a decrease in chain length, increase in chain branching, cyclization, unsaturation, and aromaticity. Furthermore, mixtures of two or more different hydrocarbons were found to exhibit ignition tendencies which were generally influenced by the more readily ignitable component [40].

5.2 Mechanism

Similarities in the effects of hydrocarbon structure on cetane number and spontaneous ignition are attributable to similarities in the physical and chemical processes that are involved in compression ignition and spontaneous ignition. The physical processes involve: transfer of heat to the droplet, vaporization of the fuel droplets to form a flammable mixture and the diffusion of fuel vapor away from the surface [15].

The chemical processes involve chain reactions. These are initiated by free radicals [15, 37, 39, 46, 49-51] that are formed during thermal and oxidative decomposition of fuel molecules [15]. These chain reactions eventually result in heat release [15] via oxidation.

The time required for the physical processes to occur is termed physical delay. Chemical delay is the time required for those chemical reactions which form the critical concentrations of free radicals and other intermediates that are necessary for ignition [40]. The collective term for both types of delay is the ignition delay. However, of the two types of delay, the chemical delay has been described as being the more meaningful [40].

It is well established that vapor phase oxidation of hydrocarbons involves radical reactions and these reactions involve both the formation of peroxides and their subsequent decomposition. Consequently, it is not surprising that the effect of hydrocarbon structure on the kinetics of compression ignition and spontaneous ignition is related to the type of peroxides formed.

This effect of hydrocarbon structure is exemplified for alkanes as follows: tertiary carbons are more reactive than secondary carbons. However, the peroxides formed by oxygen attack on the tertiary carbon yield relatively stable alkyl hydroperoxides and other stable products such as ketones. In contrast, attack on secondary carbons yields less stable products which are subject to further oxidation [52-54]. Using this simplistic model, the lower cetane numbers of branched alkanes and the higher cetane numbers of straight chain alkanes may thus be explained.

6.0 EFFECT OF LOW TEMPERATURE ON IGNITION QUALITY

Cetane number is determined at room temperature (25°C). However, diesel engine operators experience most starting problems at temperatures below freezing. In an extensive research program initiated by Shell Canada during 1980-1981, the effects of low ambient temperature conditions (between approx. 0 and -15°C) on engine startability were examined [55]. Some of the results are as follows:

1. The effect of cetane number on cold engine startability was engine dependent. For example, cold engine startability was significantly influenced by fuel cetane number in the Cummins NTC-350 engine, but not in the Detroit Diesel 8V92T-A, which is an easier engine to start.

2. In the Cummins NTC-350 engine:

   a) For fuels of approximately the same cetane number, but differing in volatilities, the low volatile fuel required longer cranking times than the high volatile fuel.
   b) At the same cetane number, natural diesel fuels provided superior starting to fuels containing ignition improvers.

In a more recent study on the effects of fuel properties on the unaided cold starting of a two-cycle diesel engine (Detroit Diesel 4-53T), Montemayor and Owens [56] observed the following: cetane number, viscosity, 50%

distillation temperature, and autoignition temperature had statistically significant impact on the Minimum Unaided Starting Temperature (MUST). The prediction equation for MUST being:

$$\text{MUST} = 32.5445 + 8.6660 * \text{Viscosity} - 0.1423 * \text{T50} - 0.6968 * \text{CN} + 0.0541 * \text{Autoignition Temp} \quad (33)$$

where: MUST is in °C; T50 is based on ASTM D2887 and autoignition temperature °C, is based on ASTM E659. Fuels that experienced fuel delivery (flow) problems or would not start at room temperature were not included in the analyses.

7.0 CONCLUSIONS

1. Problems of poor repeatability and reproductibility associated with the standard method of determining cetane number (ASTM D613), emphasize the need for an accurate and reliable method of determining cetane number. This is especially important, since cetane number is **the standard** used in evaluating cetane indices.

2. The many advantages of the throttle to misfire method of determining cetane number warrant its further investigation as a possible alternative engine test method to ASTM D613.

3. The need for continuing revisions of the calculated cetane index, ASTM D976, are indicative of fuel compositional changes arising from changes in either crude stocks, or refinery operations, or both.

4. Ingham's equation, which is currently being balloted for replacing ASTM D976-80, is somewhat more complicated than D976-80. In general, the parameters employed in both equations are fairly similar i.e., density and distillation temperature. However, Ingham's equation requires 3 distillation temperatures (viz, 10, 50, and 90%) versus the 50% of D976-80. Advantages of the 10, 50, and 90% distillation temperatures are likely due to these parameters being bulk properties related to molecular size.

5. Although the National Research Council of Canada (NRCC) cetane index was found to be a better predictor of cetane number than Ingham's equation referred to in conclusion 4. above, the complexity of this equation detracts from its merits. Nevertheless, in spite of its complexity, this equation is meaningful in that it correlates certain functions of physical properties, which are related to compositional analysis, with cetane number.

6. Physical properties which appear to contribute to good correlation of cetane index with cetane number include the combination of density and distillation temperatures. As a single predictor, aniline point is also good. Furthermore, inclusion of aniline point in a CI equation has been found to improve a cetane index involving density and distillation temperatures. However, the toxicity of aniline disfavors the use of cetane indices involving aniline point.

7. Cetane indices that are based on compositional analyses should address the variations in fuels referred to in conclusion 3. above better than those indices that are based on physical properties. Such indices should also address differences that are due to fuel type. (E. g., D976-80 is inapplicable to synthetic fuels derived from shale oils and tar sands).

8. Compositional analysis based on proton or carbon-13 NMR appears promising in the determination of cetane index. Of the cetane indices based on proton NMR compositional

analyses, the Southwest Research Institute cetane index appears particularly attractive because of its simplicity. The prediction of cetane number by group additivity and carbon-13 NMR as proposed by DeFries et al. also appears promising.

9. In spontaneous ignition tests, in general, ignition delay, self ignition point (SIP: lowest temperature for ignition and pertains to hot flames), and minimum ignition point (similar to SIP but pertains to cool flames), are inversely related to cetane number. However, good correlation between cetane number and these parameters, appears to be dependent on the hydrocarbon structure of the fuel components.

8.0 PROPOSED EXPERIMENTAL WORK (APPROACH 2)

1. Examine those methods (see Section 4) which appear most promising with respect to accuracy and simplicity. Methods which best meet these criteria are as follows:

   a. Of the various cetane indices:
      i. Ingham's cetane index (equation 19)
      ii. CGSB Cetane Index (equation 15)
      iii. Various improved cetane indices (see equations 8 and 12)
   b. Of the various methods based on molecular structure, the equation proposed by Bailey et al. [30] for fuels containing some aromatics (see equation 30) is much simpler than the best equation of GÜlder and Glavincevski [7] (see equation 29).
   c. For the determination of spontaneous ignition, Azev et al.'s method [42], in which a modified Moore instrument was used.

2. To test the various methods/correlations stated in 1. above:

   a. Use test fuels with a wide range of cetane numbers (~25 to 50).
   b. Create a data base of all fuels with respect to the following:

      i. Cetane Number ASTM D613

ii. Physical properties: API gravity, density, viscosity, aniline point, 10%, 50% and 90% distillation temperatures, and hydrogen content.

iii. Fuel composition and molecular structure with reference to hydrogen type and carbon type.

iv. Autoignition temperature.

3. Compare the predicted cetane number values determined using the methods stated in 1 above, with cetane number, as well as with the calculated cetane index (equations 3 or 4, Section 4).

4. If possible, develop new correlations for cetane number, using the following:

a. The database described earlier.

b. Simpler measurements such as refractive index.

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